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(54) **Polymer for fuel tanks**

(57) A fuel tank for a vehicle is disclosed, comprising at least one component which is injection-moulded multimodal polyethylene resin having a polydispersity  $M_w/M_n$  of at least 3. Preferably the polyethylene resin is bi-

modal, and the injection-moulded component forms one or more of the walls of the tank.

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## Description

[0001] The present invention relates to an automobile fuel tank comprising polyethylene and to the manufacture of such a tank.

[0002] Automobile fuel tanks comprising high density polyethylene are known. Such fuel tanks are typically produced by blow moulding. However, a problem with the blow moulding process is that it imposes a restriction on the shape and dimensions of the tank which can be produced. In particular, blow moulding does not permit additional features such as pipes for transferring fuel into and out of the tank to be integrally moulded with the tank body; such pipes need to be welded onto the tank after the blow moulding process. This incurs additional cost and labour, and there is the possibility of weld failure, leading to escape of fuel or vapours from the tank.

[0003] Plastics automobile fuel tanks are required to exhibit high safety performance, particularly with regard to fire resistance and impact resistance. Such fuel tanks are required to meet minimum statutory industry specified performance criteria both with respect to creep resistance when the tank is subjected to a fire, and crash test resistance when the tank is subjected to an impact. An automobile fuel tank for use in Europe is required to have a fire resistance and an impact resistance both complying with the respective standards defined in ECE34, Annex 5. In order to meet these standards, known blow moulded automobile fuel tanks are required by automobile manufacturers to have a minimum wall thickness of at least 3mm so as to provide sufficient impact strength and creep resistance for the fuel tank as a whole. An automobile fuel tank composed of polyethylene typically has a volume of up to about 100 litres, or even greater. Given the requirement for such volumes in combination with the need for progressively lower wall thicknesses, this places a high demand on the physical properties of the walls of the tank, both following manufacture and when used. Thus the walls of the fuel tank are required not to warp or shrink following the manufacture thereof, and are required to have a precisely defined shape and rigidity during use. Accordingly a fuel tank is required to have walls which are planar and not subjected to warpage or shrinkage on moulding, and which have good creep resistance and also good impact resistance. The use of an injection moulded process would enable far more complicated geometric structures to be produced than conventional blow moulding processes. However it has previously been believed that the physical properties discussed above would not be suitable in an injection-moulded fuel tank.

[0004] EP 1063116A discloses a fuel tank made by injection moulding, which is said to satisfy the above requirements. The tank is required to be formed of a polyethylene having a density of from 0.930 to 0.955g/cm<sup>3</sup>, a polydispersity  $M_w/M_n$  (where  $M_w$  is the average molecular weight of the polyethylene by weight and  $M_n$  is the average molecular weight of the polyethylene by number) of from 2 to 3, and a melt index  $MI_2$  of from 0.2 to 2 g/10min. EP 1063116A states that if the polydispersity is higher than 3, then as a result of the broad molecular weight distribution, the polymer chains of varying length have different relaxation characteristics during cooling following the injection of the molten resin. This can induce warpage or shrinkage in the fuel tank wall following the injection moulding process.

[0005] The polymers utilised in EP 1063116A are all monomodal. We have surprisingly discovered that if multimodal polyethylene is used, it is possible to obtain improvements in some of the physical properties relevant for a fuel tank with polydispersities above 3.

[0006] Accordingly in a first aspect, the present invention provides a fuel tank for a vehicle comprising at least one component which is injection-moulded multimodal polyethylene having a polydispersity  $M_w/M_n$  of at least 3. Preferably the injection-moulded component forms one or more of the walls of the tank. By "multimodal" polyethylene is meant polyethylene having at least two components of different molecular weights and compositions (ie comonomer content).

[0007] The polydispersity of the injection-moulded multimodal polyethylene is preferably at least 4, with the maximum preferably being 35, more preferably 24. The most preferred range is 4-24.

[0008] The polyethylene is preferably bimodal: by "bimodal" is meant two components of different molecular weights, one having a higher relative molecular weight than the other of the two components and compositions (ie comonomer content).

[0009] The unformulated polyethylene resin, before the incorporation of any additives, preferably has a density of from 930 to 965 kg/m<sup>3</sup>. If following injection moulding the density is lower than 930 kg/m<sup>3</sup>, then the creep resistance of the component may be insufficient for use in an automobile fuel tank. If the density is higher than 965 kg/m<sup>3</sup>, then the walls of the tank may be too brittle, resulting in insufficient impact resistance and toughness. In this specification, the density of the polyethylene is measured according to ISO 1183. Resins used in fuel tanks typically contain about 0.5wt% of carbon black, which increases the density compared with unformulated resin by less than 1 kg/m<sup>3</sup>.

[0010] The high load melt index (HLMI) of the resin is preferably between 1 and 30, more preferably between 8 and 25 g/10min. HLMI is measured using the procedures of ASTM D-1238 at 190°C using a load of 21.6kg.

[0011] For injection-moulding, an important parameter of the resin is its viscosity at high shear rate. Accordingly it is preferred that the value of  $\mu_3$ , the viscosity at a shear rate of 1000 s<sup>-1</sup>, with a die having a ratio of length to internal diameter of 15:1, is less than 7000 dPa.s, preferably less than 5000 dPa.s.

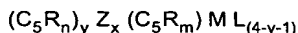
[0012] The bimodal polyethylene preferably comprises 30-70% of a low molecular weight block, and 70-30% of a high molecular weight block. Most preferred is 45-65 % of the low molecular weight block, and 55-35 % of the high

molecular weight block. The low molecular weight block is preferably a homopolymer of ethylene, but may also be a copolymer. The high molecular weight block is preferably a copolymer of ethylene and one or more of butene, pentene, hexene and octene. The Melt Index ( $MI_2$ ) of the low molecular weight block is preferably less than 1000, more preferably less than 800 and most preferably less than 200 g/10 min.  $MI_2$  is measured using the procedures of ASTM D-1238 at 190°C using a load of 2.16kg. The HLMI of the high molecular weight block is preferably between 0.001 and 2, more preferably between 0.01 and 0.7; its density is preferably less than 950, more preferably less than 940 kg/m<sup>3</sup>.

[0013] The polyethylene resin utilised in the present invention may be made using a Ziegler-Natta catalyst. In such a case, the polydispersity of the injection-moulded multimodal polyethylene is preferably between 10 and 24. Ziegler-Natta catalysts typically consist of two main components. One component is an alkyl or hydride of a Group I to III metal, most commonly  $Al(Et)_3$  or  $Al(iBu)_3$  or  $Al(Et)_2Cl$  but also encompassing Grignard reagents, n-butyllithium, or dialkylzinc compounds. The second component is a salt of a Group IV to VIII transition metal, most commonly halides of titanium or vanadium such as  $TiCl_4$ ,  $TiCl_3$ ,  $VCl_4$ , or  $VOCl_3$ . The catalyst components when mixed, usually in a hydrocarbon solvent, may form a homogeneous or heterogeneous product. Such catalysts may be impregnated on a support, if desired, by means known to those skilled in the art and so used in any any of the major processes known for coordination catalysis of polyolefins such as solution, slurry, and gas-phase. In addition to the two major components described above, minor amounts of other compounds (typically electron donors) may be added to further modify the polymerisation behaviour or activity of the catalyst.

[0014] It is preferred that the polyethylene resin is made using a metallocene catalyst, in which case the polydispersity of the injection-moulded multimodal polyethylene is preferably between 5 and 12.

[0015] Metallocenes may typically be represented by the general formula:



where  $(C_5R_n)_y$  and  $(C_5R_m)$  are cyclopentadienyl ligands,

R is hydrogen, alkyl, aryl, alkenyl, etc.

M is a Group IVA metal

Z is a bridging group,

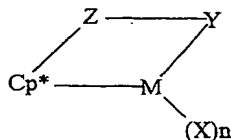
L is an anionic ligand, and

y is 0, 1 or 2, n and m are from 1 to 5, x is 0 or 1.

[0016] The most preferred complexes are those wherein y is 1 and L is halide or alkyl. Typical examples of such complexes are bis (cyclopentadienyl) zirconium dichloride and bis (cyclopentadienyl) zirconium dimethyl. In such metallocene complexes the cyclopentadienyl ligands may suitably be substituted by alkyl groups such as methyl, n-butyl or vinyl. Alternatively the R groups may be joined together to form a ring substituent, for example indenyl or fluorenyl. The cyclopentadienyl ligands may be the same or different. Typical examples of such complexes are bis(n-butylcyclopentadienyl) zirconium dichloride or bis (methylcyclopentadienyl) zirconium dichloride.

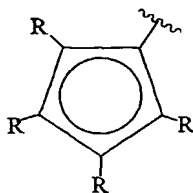
[0017] Examples of such complexes may be found in EP 129368 and EP 206794 the disclosures of which are incorporated herein by reference.

[0018] Another type of metallocene complex is constrained geometry complexes in which the metal is in the highest oxidation state. Such complexes are disclosed in EP 416815 and WO 91/04257 both of which are incorporated herein by reference. The complexes have the general formula:



wherein:

Cp\* is a single  $\eta^5$ -cyclopentadienyl or  $\eta^5$ -substituted cyclopentadienyl group optionally covalently bonded to M through -Z-Y- and corresponding to the formula:



wherein each R is independently hydrogen or a moiety selected from halogen, alkyl, aryl, haloalkyl, alkoxy, aryloxy, silyl groups, and combinations thereof of up to 20 non-hydrogen atoms, or two or more R groups together form a fused ring system;

M is zirconium, titanium or hafnium bound in an  $\eta^5$  bonding mode to the cyclopentadienyl or substituted cyclopentadienyl group and is in a valency state of +3 or +4;

each X is independently hydride or a moiety selected from halo, alkyl, aryl, silyl, germyl, aryloxy, alkoxy, amide, siloxy, and combinations thereof (e.g. haloalkyl, haloaryl, halosilyl, alkaryl, aralkyl, silylalkyl, aryloxyaryl, and alkoxyalkyl, amidoalkyl, amidoaryl) having up to 20 non-hydrogen atoms, and neutral Lewis base ligands having up to 20 non-hydrogen atoms;

n is 1 or 2 depending on the valence of M;

Z is a divalent moiety comprising oxygen, boron, or a member of Group 14 of the Periodic Table of the Elements; and

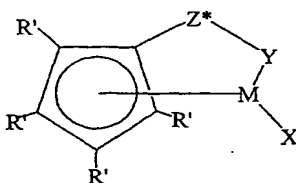
Y is a linking group covalently bonded to the metal comprising nitrogen, phosphorus, oxygen or sulfur, or optionally Z and Y together form a fused ring system.

**[0019]** Most preferred complexes are those wherein Y is a nitrogen or phosphorus containing group corresponding to the formula  $(-NR^1)$  or  $(-PR^1)$  wherein  $R^1$  is  $C_1$ - $C_{10}$  alkyl or  $C_6$ - $C_{10}$  aryl and wherein Z is  $SiR''_2$ ,  $CR''_2$ ,  $SiR''_2SiR''_2$ ,  $CR''=CR''$  or  $GeR''_2$  in which  $R''$  is hydrogen or hydrocarbyl.

**[0020]** Most preferred complexes are those wherein M is titanium or zirconium.

**[0021]** Further examples of metallocene complexes are those wherein the anionic ligand represented in the above formulae is replaced with a diene moiety. In such complexes the transition metal may be in the +2 or +4 oxidation state and a typical example of this type of complex is ethylene bis indenyl zirconium (II) 1,4-diphenyl butadiene. Examples of such complexes may be found in EP 775148A and WO 95/00526 the disclosures of which are incorporated herein by reference.

**[0022]** For example the complexes may have the general formula:



wherein:

$R'$  each occurrence is independently selected from hydrogen, hydrocarbyl, silyl, germyl, halo, cyano, and combinations thereof, said  $R'$  having up to 20 non hydrogen atoms, and optionally, two  $R'$  groups (where  $R'$  is not hydrogen, halo or cyano) together form a divalent derivative thereof connected to adjacent positions of the cyclopentadienyl ring to form a fused ring structure;

X is a neutral  $\eta^4$ -bonded diene group having up to 30 non-hydrogen atoms, which forms a  $\pi$ -complex with M;

Y is  $-O-$ ,  $-S-$ ,  $-NR^*$ ,  $-PR^*$ ;

M is titanium or zirconium in the +2 formal oxidation state;

$Z^*$  is  $SiR^*_2$ ,  $CR^*_2$ ,  $SiR^*_2SiR^*_2$ ,  $CR^*_2CR^*_2$ ,  $CR^*=CR^*$ ,  $CR_2SiR^*_2$ , or  $GeR^*_2$ ; wherein:

$R^*$  in each occurrence is independently hydrogen, or a member selected from hydrocarbyl, silyl, halogenated alkyl, halogenated aryl, and combinations thereof, said  $R^*$  having up to 10 non-hydrogen atoms, and optionally, two  $R^*$  group from  $Z^*$  (when  $R^*$  is not hydrogen), or an  $R^*$  group from  $Z^*$  and an  $R^*$  group from Y form a ring system.

**[0023]** We have found that by utilising the above-described resins, it is possible to obtain injection-moulded fuel tanks having excellent fire resistance and creep resistance, and also satisfactory impact properties.

[0024] Fuel tanks manufactured in accordance with the invention typically comprise two or more injection-moulded components joined together, for example by welding, to form an entire fuel tank. Typically, each injection moulded polyethylene resin component comprises a fuel tank half and the two halves are welded together to form an entire fuel tank. Further components may be incorporated into the tank, either made of injection-moulded polyethylene in accordance with the invention, or made of other materials.

## EXAMPLES

### EXAMPLES 1-7 - Preparation of polyethylene bimodal resin by flake blending A: Bench scale preparation of the Low Molecular Weight (LMW) Polyethylene Fraction

[0025] Under a stream of dry nitrogen gas 1.8 millimole of tri-isobutyl aluminium (TIBAL) and 1800 ml of isobutane were introduced into a dry autoclave reactor having a volume of 5 litres and provided with an agitator. The temperature was raised to 80°C, and after pressure stabilisation hydrogen gas was added. Ethylene gas was then introduced until a partial pressure of ethylene of  $10 \times 10^5$  Pa was achieved. The amount of hydrogen previously introduced into the autoclave reactor was selected so as to obtain the desired final gas phase molar ratio of hydrogen to ethylene ( $H_2/C_2$  molar ratio).

[0026] The polymerisation was then started by flushing the solid catalyst A, ethylene bis (4,5,6,7-tetrahydro-1-indenyl) zirconium dichloride (prepared in accordance with the method of Brintzinger as published in the Journal of Organometallic Chemistry 288 (1995) pages 63 to 67), into the autoclave with 200 ml of isobutane. The temperature, partial pressure of ethylene, and the  $H_2/C_2$  ratio were kept constant over the polymerisation period. The reaction was stopped by cooling and then venting the reactor. The low molecular weight polyethylene was then collected from the reactor.

[0027] The detailed polymerisation conditions are specified in Table 1.

### B: Bench scale preparation of the High Molecular Weight (HMW) Polyethylene Fraction

[0028] The process for preparing the high molecular weight fraction was the same as that for preparing the low molecular weight fraction specified above in Example A, except that instead of adding hydrogen after raising the temperature to 80°C, varying amounts of 1-hexene comonomer were added and a different amount of ethylene was introduced, in order to obtain the desired ethylene partial pressure and  $C_6=C_2$  ratio. The high molecular weight ethylene-hexene copolymer obtained was collected from the reactor.

[0029] The detailed polymerisation conditions are specified in Table 1A.

[0030] Fuel tank according to any preceding claim, wherein the polyethylene resin is made using

### C: Preparation of the Polyethylene Resin Blend

[0031] In order to prepare the bimodal resin, the desired quantity of the low molecular weight polyethylene fraction obtained in Example A above was blended with the desired quantity of the high molecular weight ethylene-hexene copolymer obtained in Example B together with Irganox B225 antioxidant commercially available from CIBA Speciality Chemicals. The resulting blend was pelletised in an extruder (APV Baker under the trade name MP19TC25). The details of the blending recipes are specified in Table 2.

### EXAMPLE 8 - Preparation of polyethylene bimodal resin by cascade reactor process

[0032] The manufacture of a polyethylene resin comprising a blend of low molecular weight and high molecular weight ethylene polymers was carried out in suspension in isobutane in two loop reactors connected in series.

[0033] Isobutane, ethylene, hydrogen, triisobutyl aluminium (TIBAL) and catalyst A were continuously introduced into the first loop reactor and the polymerisation of ethylene was carried out in this mixture in order to form the low molecular weight homopolymer. The polymerisation conditions are specified in Table 1B. The mixture, additionally comprising the low molecular weight homopolymer, was continuously withdrawn from the first loop reactor and was subjected to a reduction in pressure, so as to remove the hydrogen. The resulting mixture was then continuously introduced into a second loop reactor serially connected to the first loop reactor together with ethylene, 1-hexene and isobutane. The polymerisation of the ethylene and 1-hexene was carried out therein in order to form the high molecular weight copolymer. The suspension comprising the polyethylene resin blend of the low molecular weight and high molecular weight ethylene polymer fractions was continuously withdrawn from the second loop reactor. The suspension was subjected to a final reduction in pressure, so as to evaporate the isobutane and the remaining reactants present (ethylene, 1-hexene and hydrogen) and to recover the polyethylene resin in the form of a powder, which was subject to drying in order to complete the degassing of the isobutane. The polymerisation conditions in the second reactor are

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also specified in Table 1B.

TABLE 1A -

polymerisation conditions Examples 1-7			
Ex.	LMW block	HMW block	
	H <sub>2</sub> /C <sub>2</sub> gas phase ratio	C <sub>2</sub> partial pressure (bar)	1-hexene content (g)
1	1.58	16	70
2	1.19	6	25
3	2.1	12	27
4	2.54	12	50
5	3.17	10	20
6	3.17	8	30
7	3.29	12	34

TABLE 1B -

polymerisation conditions Example 8		
	Reactor 1	Reactor 2
T (°C)	80.0	75.0
Residence time (h)	1.5	1.0
%Ethylene	6.3	11.6
H <sub>2</sub> /C <sub>2</sub> ratio (mol%)	0.074	
C <sub>6</sub> /C <sub>2</sub> ratio (mol%)	-	8.5
H <sub>2</sub> feedrate (g/h)		0.2

TABLE 2 -

Proportions and properties of blocks of polymer for flake blending						
Ex.	LMW block			HMW block		
	wt%	MI <sub>2</sub> g/10 min	Density g/cm <sup>3</sup>	wt%	HLMI g/10 min	Density g/cm <sup>3</sup>
1	60	25	966.0	40	0.11	913.4
2	66	2.8	960.0	34	0.72	921.2
3	58	71	969.9	42	0.07	920.2
4	52	191	972.4	48	0.22	914.6
5	54	359.1	973.5	46	0.07	924.2
6	48	359.1	973.5	52	0.52	918.8
7	55	271	972.3	45	0.08	918.7

TABLE 3 -

Properties of bimodal polymer										
Ex.	MI <sub>5</sub> g/10 min	HLMI g/10 min	Density g/cm <sup>3</sup>	μ <sub>0</sub> dPa.s	μ <sub>2</sub> dPa.s	μ <sub>3</sub> dPa.s	Mn	Mw	Mz	MWD
1	0.62	16.1	944.9	246100	20400	4700	27.4	196.6	753.3	7.2
2	0.97	14.1	946.0	187100	25100	7600	37.3	154.8	468.0	4.1
3	0.51	17.5	949.9	279800	18500	3700	22.3	209	815.4	9.4
4	0.54	17.4	944.2	267500	18500	3500	18.8	194.8	727.1	10.3
5	0.25	17.5	953.4	382600	19100	3300	16.0	230.7	896.5	14.4
6	0.67	18.2	945.1	239700	18600	3700	17.5	171.7	588.4	9.8
7	0.32	13.8	949.0	347700	19300	3500	17.9	223	855.6	12.4
8	0.38	17.2	954.5	317500	16700	2800	11.8	176.7	680.1	14.9

Notes: μ<sub>0</sub> = Viscosity at shear rate of 1 s<sup>-1</sup> with a 30/2 ratio die.

μ<sub>2</sub> = Viscosity at shear rate of 100 s<sup>-1</sup> with a 30/2 ratio die.

μ<sub>3</sub> = Viscosity at shear rate of 1000 s<sup>-1</sup> with a 30/2 ratio die.

#### Physical properties for fuel tank use

[0034] For the various physical property evaluations, compressed plates of varying thicknesses were formed as follows. Polymer flake prepared as in Examples 1-8 was loaded into a picture-frame mould and brought in contact with the plates of a hot press, which were rapidly heated up to 190°C at a pressure of 20 bar. The sample was held at those conditions for approximately 5 minutes. The pressure was increased to 80 bar in order to force the polymer to flow out through the shape of the frame. After 5 minutes, pressure was released and the temperature was decreased at a rate of 15°C/min down to 35°C. The plates thus obtained were stored at room temperature for at least 7 days before being submitted to any mechanical tests.

[0035] Impact properties were assessed by notched Charpy tests performed at - 40°C on specimens taken from 4mm thick compressed plates according to ISO179/1EA.

[0036] Creep resistance was assessed by tensile strength measurements performed at 80°C under 2.5 Mpa on ISOB1A specimens machined from 2mm thick compressed plates, and is given as % deformation after 100 hours.

[0037] The results of the above tests are shown in Table 4 below. For commercial purposes, a Charpy impact of greater than 5 kJ/m<sup>2</sup> is required, and a creep of less than 2.4%.

[0038] The results of the above tests are shown in Table 4 below. For commercial purposes, a Charpy impact of greater than 5 kJ/m<sup>2</sup> is required, and a creep of less than 2.4%.

TABLE 4 -

Properties of bimodal polymer for fuel tank application		
Example	Charpy kJ/m <sup>2</sup>	Creep %
1	7.91	2.86
2	7.11	2.60
3	7.13	2.41
4	10.16	2.91
5	7.44	2.29
6	9.15	2.70
7	8.12	2.37
8	4.6	

Claims

1. Fuel tank for a vehicle comprising at least one component which is injection-moulded multimodal polyethylene resin having a polydispersity  $M_w/M_n$  of at least 3.
2. Fuel tank according to claim 1, wherein the polyethylene resin is bimodal.
3. Fuel tank according to claim 1 or 2, wherein the injection-moulded component forms one or more of the walls of the tank.
4. Fuel tank according to any preceding claim, wherein the polydispersity of the polyethylene resin is at least 4.
5. Fuel tank according to any preceding claim, wherein the unformulated polyethylene resin, before the incorporation of any additives, has a density of from 930 to 965 kg/m<sup>3</sup>.
6. Fuel tank according to any preceding claim, wherein the high load melt index (HLMI) of the polyethylene resin is between 1 and 30 g/10min.
7. Fuel tank according to any preceding claim, wherein the high load melt index (HLMI) of the polyethylene resin is between 8 and 25 g/10min.
8. Fuel tank according to any preceding claim, wherein  $\mu_3$  of the polyethylene resin, the viscosity at a shear rate of 1000 s<sup>-1</sup> with a die having a ratio of length to internal diameter of 15:1, is less than 7000 dPa.s.
9. Fuel tank according to any preceding claim, wherein the polyethylene resin is bimodal and comprises 30-70% of a low molecular weight block, and 70-30% of a high molecular weight block.
10. Fuel tank according to claim 9, wherein the low molecular weight block is a homopolymer of ethylene.
11. Fuel tank according to claim 9 or 10, wherein the high molecular weight block is a copolymer of ethylene and one or more of butene, pentene, hexene and octene.
12. Fuel tank according to any one of claims 9 to 11, wherein the Melt Index (MI<sub>2</sub>) of the low molecular weight block is less than 1000.
13. Fuel tank according to any one of claims 9 to 12, wherein the HLMI of the high molecular weight block is between 0.001 and 2.
14. Fuel tank according to any preceding claim, wherein the polyethylene resin is made using a metallocene catalyst, and the polydispersity thereof is between 5 and 12.
15. Fuel tank according to any preceding claim, wherein the polyethylene resin is made using a Ziegler-Natta catalyst, and the polydispersity thereof is between 10 and 24.





European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number  
EP 02 07 6956

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	WO 95 11264 A (MOBIL OIL CORP) 27 April 1995 (1995-04-27) * page 17, line 18; claims; examples *	1-15	C08L23/04 C08F10/02 B60K15/03
X	WO 97 02294 A (MOBIL OIL CORP) 23 January 1997 (1997-01-23) * page 4, line 27; claims; examples *	1-15	
X	EP 0 273 284 A (NIPPON OIL CO LTD) 6 July 1988 (1988-07-06) * claims; examples; tables *	1-15	
A	EP 0 645 400 A (MITSUBISHI CHEM IND) 29 March 1995 (1995-03-29) * page 2, line 11 - line 17; claims; examples; tables *	1-15	
A	PATENT ABSTRACTS OF JAPAN vol. 018, no. 511 (C-1253), 27 September 1994 (1994-09-27) -& JP 06 172594 A (NIPPON PETROCHEM CO LTD), 21 June 1994 (1994-06-21) * abstract *	1-15	TECHNICAL FIELDS SEARCHED (Int.Cl.7)
A	WO 01 14122 A (BOREALIS TECH OY ;EGGEN SVEIN (NO); NILSEN JORUNN (NO); BAANN HEGE) 1 March 2001 (2001-03-01) * claims; examples; tables *	1-15	C08F C08L B60K
D,A	EP 1 063 116 A (FINA RESEARCH) 27 December 2000 (2000-12-27) * the whole document *	1-15	
The present search report has been drawn up for all claims			
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>27 September 2002</b>	Examiner <b>Kaumann, E</b>
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
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Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9511264	A	27-04-1995	AU 692192 B2	04-06-1998
			AU 7983794 A	08-05-1995
			CA 2171019 A1	27-04-1995
			DE 69426936 D1	26-04-2001
			DE 69426936 T2	28-06-2001
			EP 0724604 A1	07-08-1996
			ES 2155095 T3	01-05-2001
			JP 9506912 T	08-07-1997
			WO 9511264 A1	27-04-1995
			US 5539076 A	23-07-1996
WO 9702294	A	23-01-1997	US 5882750 A	16-03-1999
			AU 704049 B2	15-04-1999
			AU 5789096 A	05-02-1997
			CA 2226183 A1	23-01-1997
			EP 0836623 A1	22-04-1998
			JP 11508633 T	27-07-1999
			WO 9702294 A1	23-01-1997
			US 6403181 B1	11-06-2002
EP 0273284	A	06-07-1988	JP 63154753 A	28-06-1988
			CA 1315447 A1	30-03-1993
			DE 3773631 D1	14-11-1991
			EP 0273284 A2	06-07-1988
			US 4835219 A	30-05-1989
EP 0645400	A	29-03-1995	JP 7090021 A	04-04-1995
			JP 7097408 A	11-04-1995
			DE 69409318 D1	07-05-1998
			DE 69409318 T2	12-11-1998
			EP 0645400 A1	29-03-1995
			US 5547722 A	20-08-1996
			JP 7145211 A	06-06-1995
			JP 2000063431 A	29-02-2000
JP 06172594	A	21-06-1994	NONE	
WO 0114122	A	01-03-2001	AU 6584200 A	19-03-2001
			EP 1204523 A1	15-05-2002
			WO 0114122 A1	01-03-2001
EP 1063116	A	27-12-2000	EP 1063116 A1	27-12-2000
			AU 5975600 A	31-01-2001
			WO 0100432 A1	04-01-2001
			EP 1189781 A1	27-03-2002
			JP 2001071759 A	21-03-2001

EPO FORM P0459

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